

Preliminary Sampling for Pyrethroids in Stream Sediments of Montana



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1.0 Introduction

Pyrethroids are a group of insecticides used increasingly nationwide in place of more heavily restricted organophosphates (Amweg et al., 2005). Pyrethroids are synthetic forms of pyrethrins, a natural insecticide produced by some species of chrysanthemum plants. Montana crops on which pyrethroids are commonly used include, but are not limited to, corn, sugar beets, wheat, barley and potatoes. Pyrethroids are also used extensively for urban/suburban insect and spider control.

Pyrethroids are largely insoluble, non-persistent chemicals, and therefore are not very mobile in the environment. However, they do bind tightly to the organic fractions in soils, and are therefore prone to be transported and deposited in streams along with soil particles after a rainfall event or irrigation. Once deposited in streams the pyrethroids are relatively persistent and can be toxic to aquatic macroinvertebrates at low concentrations (Gan et al., 2005). Recent studies in urban and agricultural parts of California have revealed extensive stream sediment pyrethroid contamination at levels acutely toxic to sensitive aquatic macroinvertebrate taxa (Amweg et al., 2005; Starner et al., undated and Weston et al., 2004). Amweg et al., 2005, reported average 10-day LC₅₀ for the amphipod *Hyaella azteca* for several commonly used pyrethroids in the range of 0.0045 to 0.09 µg/g in several California streams.

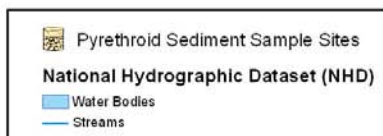
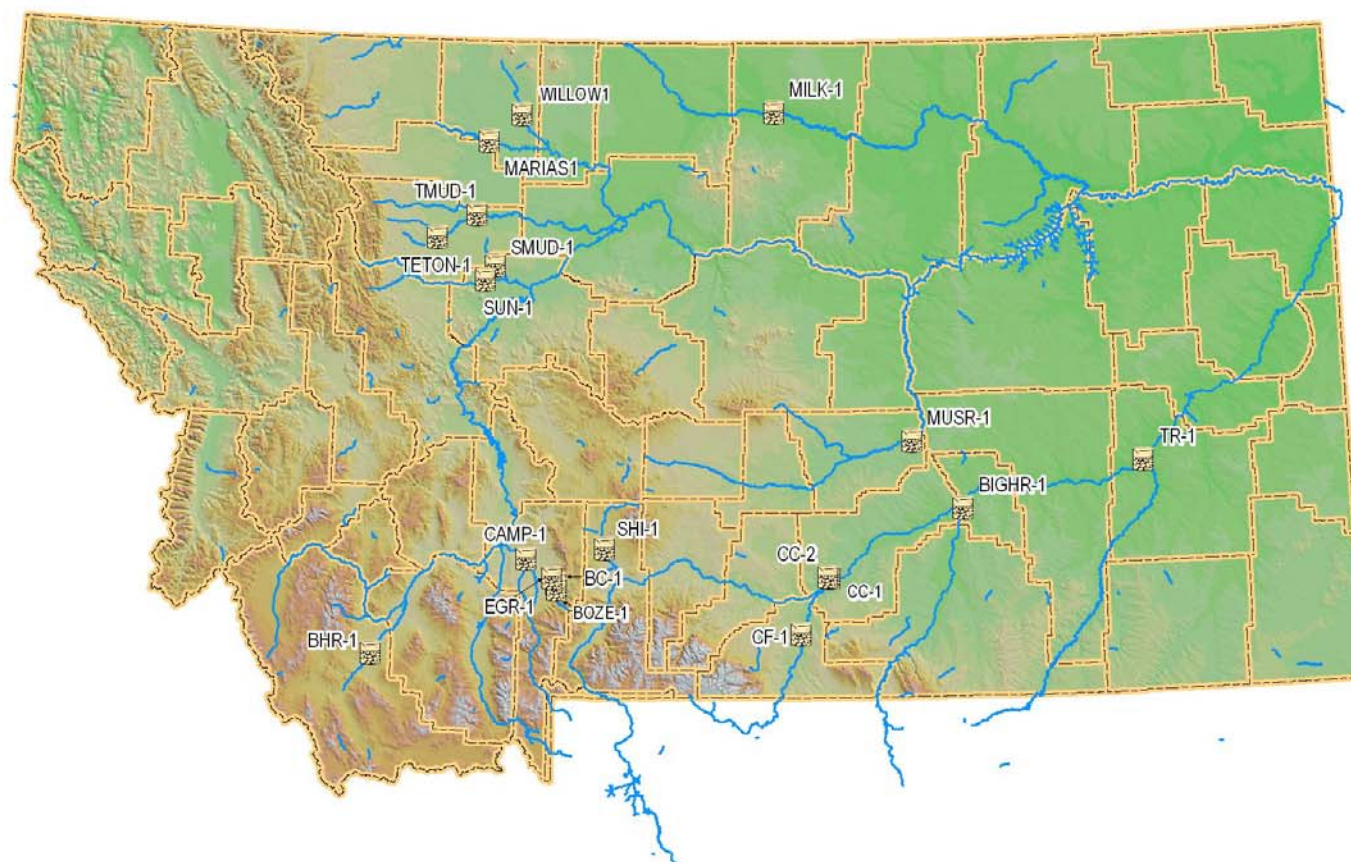
Pyrethroids that are dissolved and/or adsorbed to particles suspended in the water column may have ecosystem effects. However, available information indicates that sediment toxicity is a more significant issue for aquatic macroinvertebrate mortality, and consequently to the fish that feed on them (Amweg et al. 2005).

This report summarizes the results of sediment sampling in streams across Montana conducted by the Montana Department of Agriculture (MDA). Until this project, there has been no known sediment sampling for pyrethroids conducted in the state of Montana. A total of 20 samples from 19 sites were collected from the fall of 2006 through the summer of 2007 and analyzed for 10-14 pyrethroid compounds. No pyrethroids were detected in any of the sediment samples.

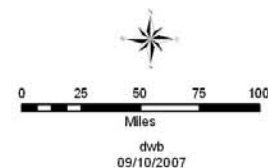
2.0 Sampling Locations and Field Methods

Sampling areas were initially located using aerial photos and local knowledge for a coarse screening, then on site reconnaissance was used to select the location. The following criteria were used to select sampling locations: 1) when and where were pyrethroid applications likely to occur; 2) where were vulnerable stream reaches located within these areas - factors considered include the distance between the stream and probable application areas, the length of stream near probable application areas, the extent of irrigation return flow from probable source areas into the stream, stream discharge, and the degree to which fine sediment is present in the stream; and 3) where was stream access possible. Sampling locations are shown on the following page.

Pyrethroid Stream Sediment Sample Sites 2007



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In October of 2006, sediment samples were collected from Bozeman Creek below Bozeman, Canyon Creek southwest of Billings, and the Clark's Fork of the Yellowstone at the town of Fromberg. In June of 2007, samples were collected from the Marias River near Shelby, Willow Creek west of Chester, the Teton River below Choteau, Muddy Creek (a Teton River tributary) north of Dutton, Bozeman Creek above Bozeman, Camp Creek near Manhattan, and the Milk River near Chinook. In July 2007, samples were collected from the Sun River at the town of Sun River, Muddy Creek (a Sun River tributary) above Valier, the Shields River above Clyde Park, the Clark's Fork of the Yellowstone at Fromberg (same site sampled in October 2006), and the Bighorn River at the Manuel Lisa Fishing Access Site, two miles from the mouth at the Yellowstone River. In August 2007, samples were collected from the Beaverhead River below Dillion, the East Gallatin River north of Bozeman, the Tongue River at Miles City, Canyon Creek southwest of Billings (different location than the sample from October 2006), and the Musselshell River near Melstone.

Pyrethroids primarily sorb to organic matter and colloidal particles. Therefore, samples were collected from recently deposited fine sediments that were preferably rich in organic matter. Three sampling environments were encountered during this project: type (1) slow stream flow with a soft bottom; type (2) relatively fast stream flow with coarse bottom material and pockets of fine material; type (3) slow stream flow with primarily coarse bottom material covered with filamentous algae and a thin layer of fine material. Different sample collection techniques were used for each environment. For type 1 environments, a trowel was used to remove the upper sediment layer (0.5 inches or less). For type 2 environments latex gloved hands were used to grab sediment from the streambed (the sediment would wash off the trowel because of the fast current). For type 3 environments, latex gloved hands were used to collect sediment from the algae and cobble surfaces. All subsamples were placed into a clean stainless steel bucket and homogenized.

All samples were put on ice immediately after collection. Samples were allowed to settle overnight and then excess liquids were decanted. Samples were then frozen prior to shipment to the laboratory.

3.0 Laboratory Analysis and Results

Three initial sediment samples collected in October of 2006 were sent to the MDA Analytical Bureau at Montana State University. These samples were analyzed for bifenthrin, cis-permethrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, deltamethrin, fenpropathrin, fenvalerate+esfenvalerate, fluvalinate, prallethrin, resmethrin, tefluthrin, tetramethrin, and trans-permethrin. Samples collected in June, July, and August of 2007 were sent to Caltest Analytical Laboratory in Napa, California, for analysis of Deltamethrin, Bifenthrin, Cyfluthrin, Cyhalothrin, Cypermethrin, Esfenvalerate, Fenpropathrin, Fluvallinate, Permethrin, and Resmethrin concentrations.

None of the samples contained pyrethroids above the analytical method reporting limits. Analytes and their corresponding reporting limits are included in the table below.

MDA Analytes and Reporting Limits (µg/g)		Caltest Analytes and Reporting Limits (µg/g)	
Bifenthrin	0.005	Bifenthrin	0.007
cis-Permethrin	0.006	Deltamethrin	0.007
Cyfluthrin	0.060	Cyfluthrin	0.007
Lambda-cyhalothrin	0.030	Cyhalothrin	0.007
Cypermethrin	0.10	Cypermethrin	0.007
Deltamethrin	0.10	Fenvalerate+esfenvalerate	0.007
Fenpropathrin	0.020	Fenpropathrin	0.007
Fenvalerate+esfenvalerate	0.030	Fluvalinate	0.007
Fluvalinate	0.20	Permethrin	0.007
Prallethrin	0.036	Resmethrin	0.007
Resmethrin	0.012		
Tefluthrin	0.0030		
Tetramethrin	0.050		
trans-Permethrin	0.012		

At each site a sample was also collected for total organic carbon (TOC). TOC samples were collected because TOC concentration is inversely related to the toxicity of sediment pyrethroids and is used in determining if deleterious concentrations are present. TOC concentrations ranged from 0.53 – 6.37%.

Sample Location (Site ID)	Total Organic Carbon
Bozeman Creek below Bozeman (BC-1)	0.60%
Canyon Creek near Billings (CC-1)	0.64%
Clarks Fork of the Yellowstone at Fromberg (CF-1)	2.17%
Marias River near Shelby (Marias-1)	2.28%
Willow Creek west of Chester (Willow-1)	1.31%
Teton River below Choteau (Teton-1)	6.37%
Muddy River north of Dutton (TMUD-1)	2.71%
Bozeman Creek above Bozeman (BOZE-1)	1.65%
Camp Creek near Manhattan (CAMP-1)	0.58%
Milk River near Chinook (MILK-1)	1.33%
Sun River at Sun River (SUN-1)	1.97%
Muddy Creek above Valier (SMUD-1)	2.18%
Shields River above Clyde Park (SHI-1)	0.53%
Bighorn River at Manuel Lisa Fishing Access Site (BIGHR-1)	2.34%
Beaverhead River below Dillon (BHR-1)	3.62%
East Gallatin River north of Bozeman (EGR-1)	0.78%
Tongue River at Miles City (TR-1)	1.24%
Canyon Creek southwest of Billings (CC-2)	2.07%
Musselshell River near Melstone (MUSR-1)	1.82%

4.0 Future Work

Although no pyrethroids were detected in the samples collected during this project, additional sampling may be warranted. This project concentrated on potential non-point source impacts of pyrethroids. Future sampling could target specific pyrethroid sources such as irrigation return flow ditches or stream reaches immediately downstream of irrigation return flow. Urban streams could be sampled immediately downstream of storm sewer discharges. Rivers with agriculture land uses along long stretches of the rivers may also warrant multiple samples from different areas instead of the single location sampled during this project.

5.0 References

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